Investigation of Oxidative Breakers for the Reduction of Health and Environmental Impacts Associated with Hydraulic Fracturing Fluids

THESIS

Presented in Partial Fulfillment of the Requirements for Graduation with Honors Research Distinction in Chemical Engineering at The Ohio State University

By

Jack Jones
B.S. Program in Biomedical Engineering

The Ohio State University
2016

Thesis Committee:
Dr. Kurt W. Koelling, Advisor
Dr. David Wood

Abstract

Hydraulic fracturing ("fracking") has long been necessary to obtain natural gas in the US and around the world. Tensions in the Middle East and dwindling oil reserves that cannot be obtained by conventional means have caused fracking to become even more popular. Unfortunately, major environmental and health concerns are now associated with the fracking process. There are fears of fracking fluid impacting quality of drinking water or natural ecosystems. During hydraulic fracturing, a slurry of chemicals is pumped into the ground with the intention of creating tiny cracks and propping these cracks open with a viscos fluid containing sand particles. The viscosity of the fluid keeps the sand from settling, but once the fracking team wants to extract gas from the well, viscosity needs to decrease so all the fracking fluid can be easily removed. Decreased viscosity is achieved by adding breaker, usually an oxidizing chemical that can break bonds in the original polymer chains that were giving the fluid its viscosity. This study aims to replace the conventional breaker, ammonium persulfate, with a less toxic oxidizing agent. Analysis of the breaking mechanism has led to novel ideas for potential replacements. Additional potential replacements were theorized from techniques used in chemical cleaning and paper industries. Rheological tests (both frequency sweeps and rate sweeps) were conducted on possible replacements to determine how they compare to ammonium persulfate in terms of decreased fluid viscosity. The impacts of temperature and concentration were further analyzed for the most viable replacements. Filter-degradation studies were conducted to quantify the relative effect of each breaker on the size of polymer residues it leaves behind. Replacements deemed viable based on degradative ability were further compared on the basic of relative toxicity and cost. Results conclude multiple possible replacements for ammonium persulfate. The most viable of these are ferrous sulfate and sodium hypochlorite. Sodium hypochlorite works as well as ammonium persulfate at lower concentration, but is highly toxic in aquatic ecosystems. Ferrous sulfate only works as well as ammonium persulfate at double the concentration, but has no known health or environmental impacts.

Acknowledgements

Thank you, to my family and friends for their constant support. You provided a much needed distraction.

Thank you, to my research advisor, Dr. Kurt Koelling, for providing me with the opportunity to pursue undergraduate research in chemical engineering, even after changing majors. I learned to be an independent and productive research scientist.

Thank you, to my instructors in chemical and biomedical engineering courses at Ohio State. You've prepared me for a future in medical fields and helped open my mind to interdisciplinary pursuits.

Thank you, to the College of Engineering, the University Honors Program, and the Kelm family. Your financial support allowed me focus more intently on academic and extracurricular pursuits.

Thank you, to my lab mentors for their assistance and friendship: Joseph Gauthier and Nicholas Ohanian

Thank you, to my past partner, Thomas Groseclose, who learning all the fundamentals with me from our mentors. He finished his thesis first and showed me something to strive for.

Vita

2012.....Olentangy Liberty High School

2016.....B.S. Biomedical Engineering, The Ohio State University

Field of Study

Major Field: Biomedical Engineering

Table of Contents

List of Figures

List of Tables

Introduction

Overview

Hydraulic fracturing, commonly known as fracking, is a method of hydrocarbon recovery that involves injecting large volumes of pressurized fluid into the earth's surface to recover oil and natural gas resources which are not easily accessible by other means [1]. The pressurized fluid opens tiny cracks that allow liquid, but mostly gaseous, hydrocarbons to flow freely towards the surface for storage and future use. The pressure is eventually released and tiny sand particles called proppants prop open the cracks that have formed, so that hydrocarbons can be continually collected.

Fracturing wells typically begin by drilling a cement-lined hole to the depth of the resource being recovered (6,000-10,000 ft. downward), and adding encasing to protect groundwater (1,000-4,000 ft. downward) [2]. Temperatures at this depth are 25-150˚C [3]. Figure 1 below shows the essentials of the fracking process.

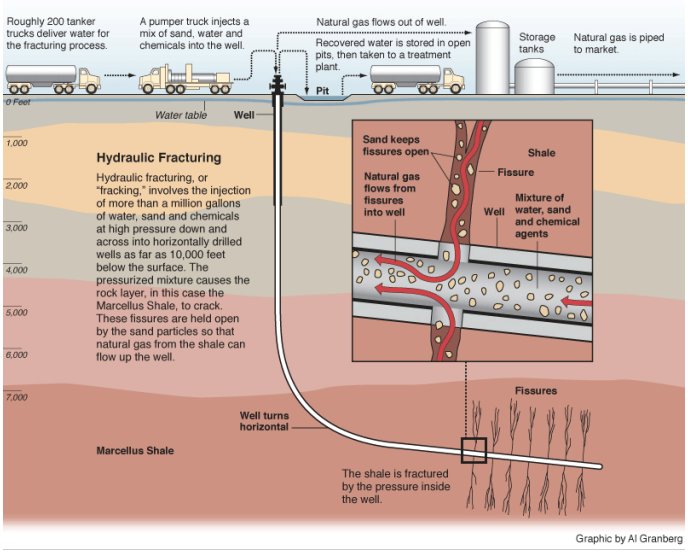

Figure 1: The hydraulic fracturing process [4]

Since sand is denser than water, additives are needed to increase the viscosity of the water, so that the sand will not quickly settle to the bottom of the well. Hydroxypropyl guar (molecular weight 10^5-10^6) is the common choice to increase viscosity [5]. Guar gum has been used in food and textile industries, and is now used in the petroleum industry [6]. The guar polymer is shown in figure 2, below. Typically, metal compounds of zirconium, boron, or titanium are used as crosslinker to further increase the viscosity of the mixture. The metal ions hold together individual chains of guar polymer to create a

network of interconnected molecules with increased molecular weight [7]. The structure of crosslinked guar is shown in Figure 3, below.

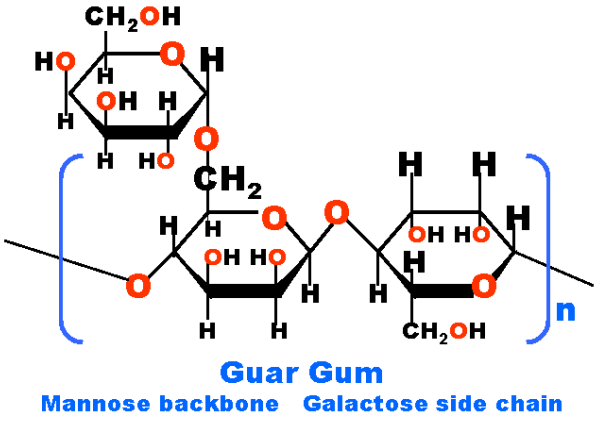

Figure 2: Repeating subunit of the guar molecule [15]

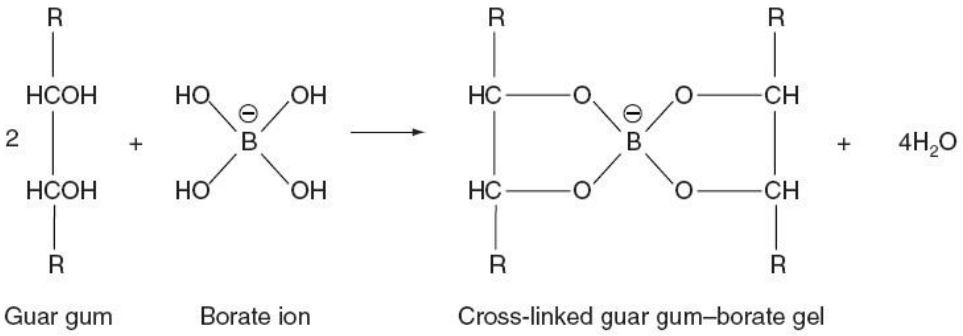

Figure 3: Mechanism of guar crosslinking with borate ion [16]

Since the crosslinked guar solution is now at very high viscosity, it would be hard to remove it from the well without first decreasing the viscosity. Breaker, most commonly ammonium persulfate, is used in small concentrations to break down guar polymer via oxidation pathways. The broken solution can be easily pumped out of the well and disposed of.

Motivation

Hydraulic fracturing is widely used in the United States and abroad to capture vital natural resources. Natural gas, the primary product of fracking, is the cleanest burning fossil fuel and is abundant enough in the United States to fuel our energy independence for another 90-115 years [1]. Of course, many people are worried about the ramifications of fracking fluids entering drinking water or

local ecosystems. Many trace chemicals in fracking fluid are dangerous. In particular, oxidative breakers, most commonly ammonium persulfate, are understood to be toxic to humans and the environment [8]. For this reason, an effort has been made to replace the conventional breaker with alternatives that are less harmful to people and the environment.

In order to replace ammonium persulfate, an alternative breaker would need to break crosslinked guar to the same degree as ammonium persulfate when added in equal concentration. Rheological testing was conducted to determine viscoelastic properties of solutions broken by various breakers. Additionally, filter-degradation studies were conducted to determine the permeability of various broken solutions. Solutions broken with alternative breakers need to filter as effectively as solutions broken with ammonium persulfate, because the overall size of polymer molecules after breaking determines how much residue will be left down-well. Larger polymer fragments lead to a higher residue percent and lower well efficiency.

A potentially replacement to ammonium persulfate needs to compete with the conventional breaker not only in terms of breaker ability/effectiveness, but also in terms of cost and overall hazard potential. Effective breakers were compared to ammonium persulfate in terms of bulk cost and associated dangers from Safety Data Sheets.

Ammonium persulfate and potential replacements

To determine which types compounds may present potential alternatives to ammonium persulfate, it's necessary to understand how ammonium persulfate functions as a breaker. Most breakers used in industry are strong oxidizers that break down guar by free-radical oxidation mechanisms [9]. Figure 4 illustrates how ammonium persulfate degrades guar. A single sub-unit of guar has 18 available sites that could be deprotonated by this mechanism, as displayed in Figure 5.

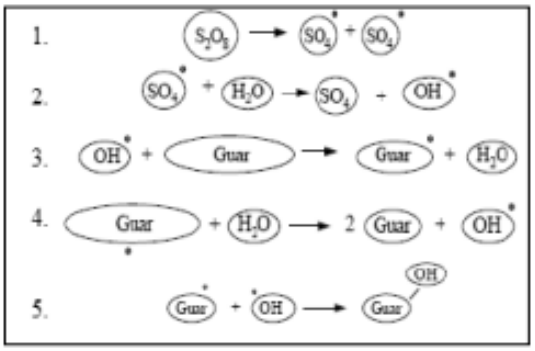

Figure 4: Steps in the proposed oxidative free-radical mechanism of guar degradation [5]

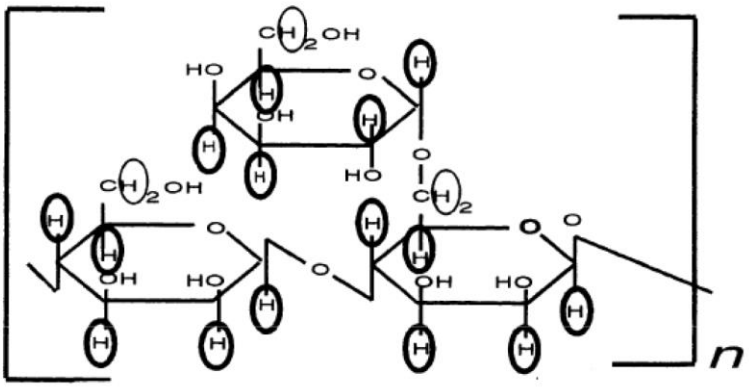

Figure 5: Circles around each of the 18 protons that could be removed by the free-radical oxidation mechanism [10]

In terms of maximized breaking, the best sites to degrade in step 3 of Figure 4 would be those of the β-1, 4 acetal linkages between the mannose units. This would create two equal-sized polymer chains, maximizing the molecular weight reduction. Unfortunately these hydrogens are less acidic than the rest, so they have lesser affinity for the oxidation mechanism [3]. It's likely the guar polymer is split unevenly, creating one larger and one smaller polymer chain. Regardless, it is assumed that ammonium persulfate is able to decrease both bulk viscosity and individual fragment size to a point deemed useful for fracking purposes.

Ammonium persulfate and the potential breaker replacements are listed by name and chemical structure in Figure 6 below.

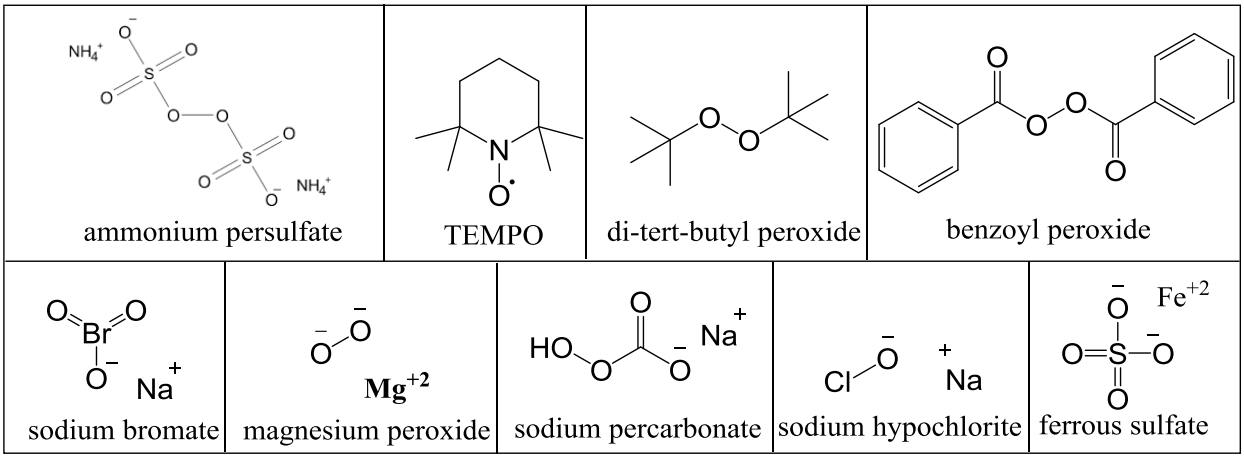

Figure 6: Chemical structures of each breaker analyzed

Replacements such as Sodium Bromate (Sigma-Aldrich) and Magnesium Peroxide (Aldrich Chemistry) were tested because these appeared in Sarwar's thesis which attempts to replace ammonium persulfate and was the basis for many of the methods in this study. These breakers are most active in a temperature ranges above 200˚C, but may have some lesser activity at lower temperatures [3].

Compounds such as di-tert-butyl peroxide (Aldrich Chemistry), benzoyl peroxide (Aldrich Chemistry), and TEMPO (Aldrich Chemistry) were proposed because these readily form oxygen radicals that may work by the same mechanism the ammonium persulfate radical. Figure 7 shows each of these compounds in radical forms.

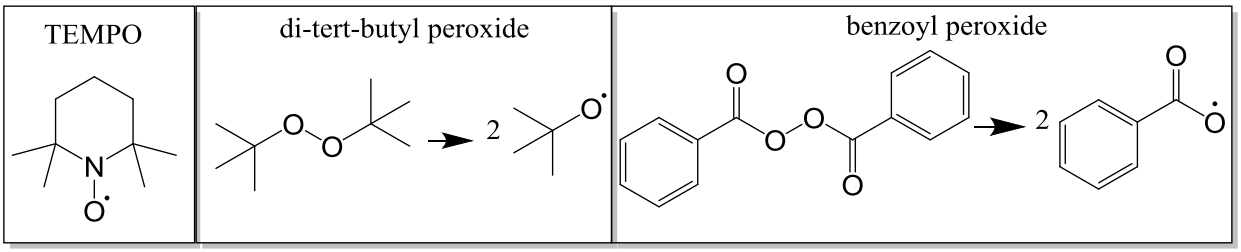

Figure 7: Oxygen radicals formed by selected breaker compounds

TEMPO is a stable chemical radical used in biological and biochemical applications. Both di-tert-butyl peroxide and benzoyl peroxide readily break down into radicals with heat or light. Both are commonly used as initiators in polymerization chain reactions, but may serve the opposite purpose in this case.

Compounds such as sodium percarbonate (Aldrich Chemistry) and sodium hypochlorite (Fischer Scientific) were selected because they are strong oxidizers. These compounds are used as oxidizers in commercial and domestic bleaching processes [10]. Sodium percarbonate is the active ingredient in Oxi-clean, whereas sodium hypochlorite is the active ingredient in household bleach.

Ferrous sulfate (Sigma-Aldrich) was originally intended to catalyze peroxide reactions via Fenton chemistry, but was found to also break guar by itself. In the Fenton reaction, aqueous iron in the +2 oxidation state can react with peroxide to generate radicals more abundantly than heat or light alone [11]. Mn^{+2} has also been shown to generate radicals, and it has been found that Mn^{+2} can oxidize cellulose directly, lending credence to the idea that Fe^{+2} can directly oxidize guar [12]. Any Fe^{+2} compound could be used, but ferrous sulfate was used since the sulfate ion will not obstruct hydrogen ions. The sulfate ion is the conjugate base of a strong acid. Fenton chemistry and oxidative breaking in general are best conducted at low pH [3].

Experimental Methods

Overview

Experiments were conducted with industrial hydraulic fracturing operations in mind. Concentrations were determined from literature and industry sources. FracFocus is an online chemical disclosure website that lists chemicals and concentrations used in real fracking wells. Guar was generally used at roughly 0.5% by weight. Sodium tetraborate crosslinker is found in 0.08% to 0.2% by weight, so 0.2% was chosen to show the greatest crosslinking effect compared to non-crosslinked guar. Ammonium persulfate breaker is typically used in 0.01% to 0.1% by weight, so 0.1% was chosen to show the greatest possible degradation. Possible alternative breakers were tested at this same weight percent.

All solutions were made from distilled water and were mixed at 500 rpm by a magnetic stir rod. Guar powder (Tiguar 418, SOLVAY) and water were stirred for at least one hour before crosslinker was added. Sodium tetraborate decahydrate (Fischer Scientific) crosslinker was stirred for at least eight hours before any breaker was added. The amount of time needed to fully break solutions with ammonium persulfate (SANTA CRUZ BioTechnology) was determined by preliminary experimentation to be no more than 1 hour, but a break time of 24 hours was used to assure time independence for all breakers.

Solutions were made identically each time to assure repeatability. First, 0.5 grams guar was added to 99.5 mL water and stirred for one hour in a 500 mL jar. Next, the solution was split in half by measuring 50 mL into a graduated cylinder, then adding this to a second 500 mL jar. 0.1 grams sodium tetraborate crosslinker was added to one of the 50 mL solutions and it was allowed to stir for a minimum of 8 hours and a maximum of 24 hours.

Breakers were then added. 0.01 grams of any solid breaker can be added to 10 mL of either guar or crosslinked guar to achieve the 0.1 weight percent desired. Guar and crosslinked guar were transferred to 50 mL jars using a 10 mL syringe. Solutions were shaken until the breakers fully dissolved, and either kept at room temperature or heated in a water bath to 50˚C for 24 hours. Solutions were allowed to cool to room temperature before any tests were conducted. Room temperature and 25˚C are used interchangeably in this study, despite fluctuations.

Sodium hypochlorite was a 13% concentrated liquid which was added dropwise using a micropipette. This breaker is unique because the data displayed for rheological and filter-degradation

tests used only ~0.0029 weight percent (20 µL) instead of the typical 0.01 wt% for other breakers. This was because preliminary testing showed that greater concentrations actually overtook the impact of ammonium persulfate. Figure A1 in the appendix shows this anomaly. Since breakers were added as solids or concentrated solutions of tiny volumes (0.2% of the total volume), it was assumed there was no viscosity change due to dilution.

Rheological Studies

The ARES G-2 Rheometer, pictured below, was used to conduct all rheological tests. Oscillatory frequency sweep tests and steady shear rate sweep tests were conducted on each solution. Tests were conducted at room temperature and atmospheric pressure with 50 mm parallel plate geometry, shown in Figure 9.

Figure 8: Ares G-2 Rheometer

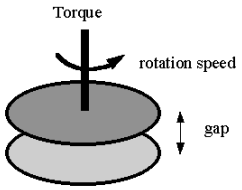

Figure 9: Parallel plate geometry [17]

Fluid is injected into the gap, then sheared by the movement of the top plate. Internal calculations based on the torque needed to move the top plate and the gap height determine viscosity and other fluid properties. The oscillatory frequency sweep test was from 0.1 to 100 rad-sec^{-1} with 20% strain. This strain percentage was determined during preliminary testing. The steady shear rate sweep

tests were conducted from 0.1 to 100 sec^{-1} with a frequency of 1 Hz. The purpose of both of these tests was to determine the viscosity of guar and crosslinked guar before and after interaction with various breakers. Each solution was tested at least twice under a given set of conditions. If results were deviant, a third test was conducted to settle the dispute. All rheological results shown in this work are selections of representative data sets after multiple rheological tests were conducted. If rate sweep and frequency sweep data were in disagreement, both tests were redone to assure each breaker's ability is properly represented. Tests take about 5 minutes to conduct, so evaporation was assumed to be minimal.

Filter-Degradation Studies

A major function of breakers, besides decreasing bulk viscosity, is significantly decreasing the molecular weight of the polymer chains. This reduces residue down-well, leading to more environmentally friendly drilling and increased well efficiency. Filter-degradation tests aim to show differences in average polymer molecular weight after breaking with the most successful breakers.

Effective breakers were used to make broken solutions at 50˚C, identical to the solutions used in rheological testing. 10 mL of each solution was generated, just as above. The solutions were dumped from 50 mL vials into a Buchner funnel vacuum filtration apparatus, which was connected by an aspirator to a faucet. Solutions filtered for 3 minutes while being rinsed with distilled water. Distilled water was used to clean residue in the vials into the filtration device. The filter paper and any residual liquid above it were moved to tin weigh-boats after three minutes, then kept in a pressurized oven set to 50˚C and 20 bar. Residue mass was determined by weight difference between the initial and final masses of weigh-boat and filter paper pairs, as to account for the weight of any large polymer chains that could not pass through the filter. The Buchner funnel was 9 cm in diameter, with Whatman Size 4 filters (20-25 µm, 37 sec/100 mL Herzberg speed).

Hazard Analysis

Toxicities of effective breakers were determined from Safety Data Sheets available online.

Cost Analysis

Bulk chemical prices of each effective breaker were determined from multiple internet sources. The lowest price for bulk, high purity breaker was determined, and then converted to standard units of US dollars/metric ton.

Results and Discussion

Rheological Studies

After determining the appropriate strain for subsequent testing, a series of frequency sweep tests were conducted between 0.1 and 100 radians-sec^{-1}. Each breaker was tested on guar and crosslinked guar at 25 and 50°C. Data before 0.2 reciprocal seconds was routinely excluded from frequency sweep tests because the low torque signal caused excessive noise. Below, Figure 10 displays only the data for crosslinked guar broken at 50°C, since this scenario is most similar to down-well conditions in an actual fracking well.

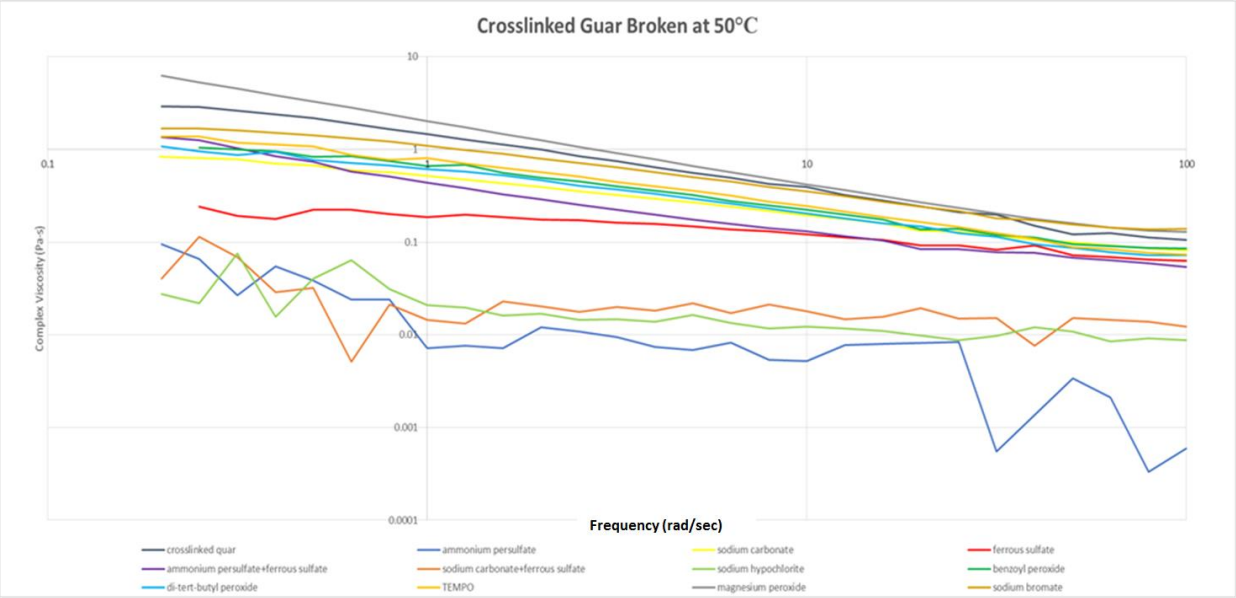

Figure 10: Frequency sweeps of breakers acting on crosslinked guar at 50˚C

Figure 11, below, shows rate sweep data for crosslinked guar broken at 50˚C. This data is meant to justify and further bolster the frequency sweep results above. Data beyond 10 reciprocal seconds was occasionally excluded for the most effective breakers because the excessively low viscosities achieved lead to rapid fluctuations.

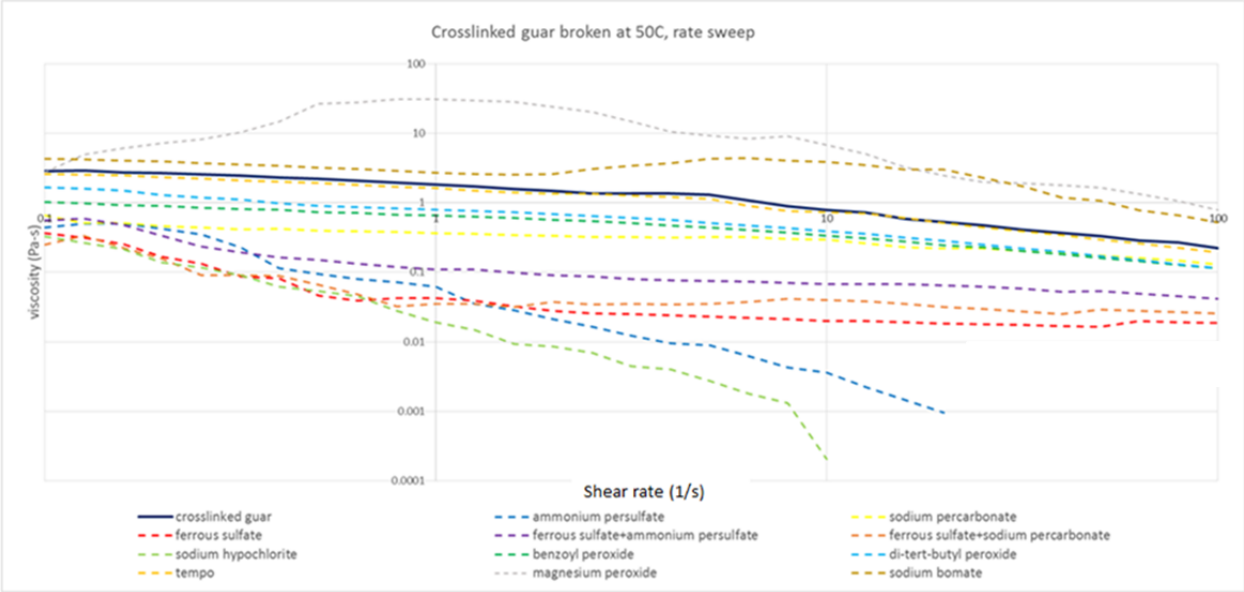

Figure 11: Rate sweeps of breakers acting on crosslinked guar at 50˚C

It is clear upon initial inspection that only sodium hypochlorite (even at only ~0.0029 wt%) and a mixture of sodium carbonate with ferrous sulfate can match the breaker ability of ammonium persulfate. Ferrous sulfate alone significantly breaks the crosslinked solution, though not to the same magnitude. Ferrous sulfate was included in the following figures because it is proportionally more active at 25°C. Ferrous sulfate produces a qualitatively different kind of break. Solutions broken with the other breakers seem like water, but solutions broken with ferrous sulfate alone display characteristics similar to water with stronger cohesion force. The ferrous sulfate broken solutions pool more easily and will not drip from the tip of a syringe. This strange anomaly is not a focus of this study, but could be responsible for the consistent discrepancy between frequency sweep tests and rate sweep tests for this suggested breaker. All other potential breakers were discarded from the following figures for easy of viewing, but full data sets can be found in the appendix. It's also interesting to note that ammonium persulfate is less active when mixed with equal weight percent ferrous sulfate. Ferrous sulfate was intended to catalyze radical formation, but clearly doesn't make ammonium persulfate more effective.

Figure 12 displays rate sweep data for each of the selected breakers acting on crosslinked guar at 25 and 50˚C. Rate sweep data is less noisy and is therefore used in the remaining figures without showing the associated frequency sweep data. Addition frequency sweep data can be viewed in the appendix. In the following figure, the impact of temperature can be better understood for each breaker. It's apparent that ferrous sulfate stands alone in being equally active at lower temperature.

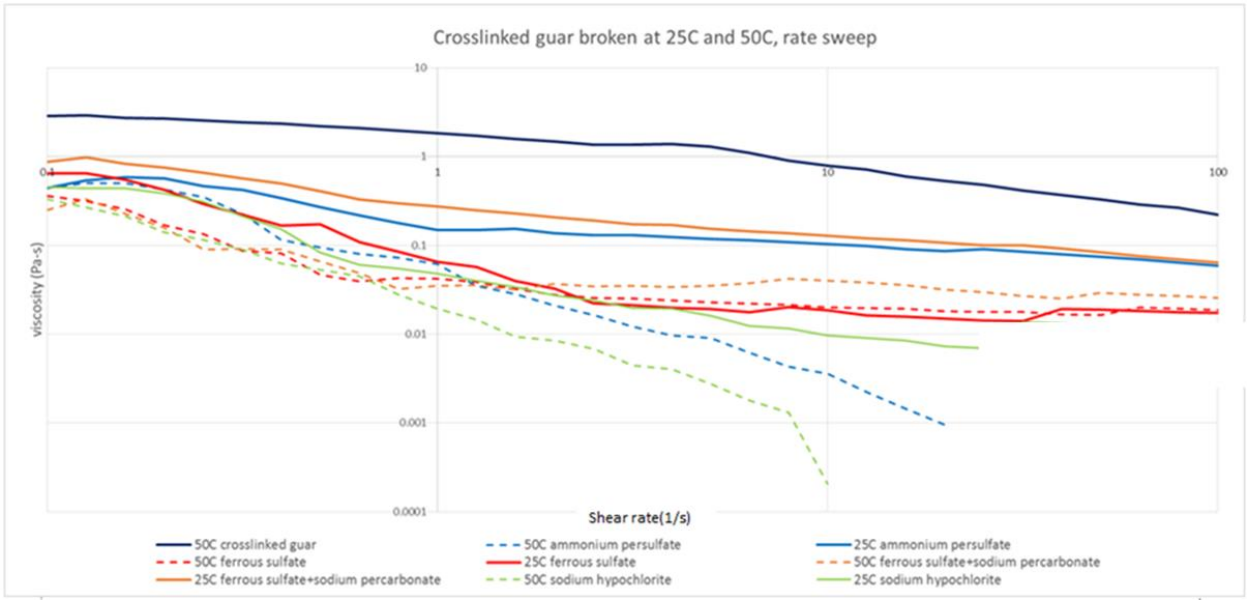

Figure 12: Rate sweep data for crosslinked guar broken at 25 and 50˚C

Figure 13 shows rate sweep data of each selected breaker acting on guar and crosslinked guar side by side at 50˚C. Data is displayed as viscosity ratios in which the final viscosities after breaking are divided by initial viscosities of either guar or crosslinked guar. This allows for examination of the relative impact of each breaker on the different polymer species as fractions of the polymers' initial viscosities.

Figure 13: Viscosity ratios of guar and crosslinked guar each broken at 50˚C, determined by rate sweep tests

Ammonium persulfate has a proportionally greater impact on guar than on crosslinked guar. The opposite is true of ferrous sulfate, which has far more proportional activity with crosslinked guar. Breaking with sodium hypochlorite displays this same trend of working proportionally better on crosslinked guar, though to a lesser extent than ferrous sulfate. The combination of ferrous sulfate and sodium percarbonate has similar activity with both crosslinked and uncrosslinked guar and is highly dependent on frequency.

Finally, Figure 14 shows each selected breaker working on crosslinked guar at double the normal concentration. Ferrous sulfate and ferrous sulfate with sodium percarbonate act at 0.2% by weight, and 40 µL sodium hypochlorite (~0.058 wt%) was used. For the mixture of sodium percarbonate with ferrous sulfate, only the concentration of sodium percarbonate was doubled, since ferrous sulfate is meant to act as a catalyst.

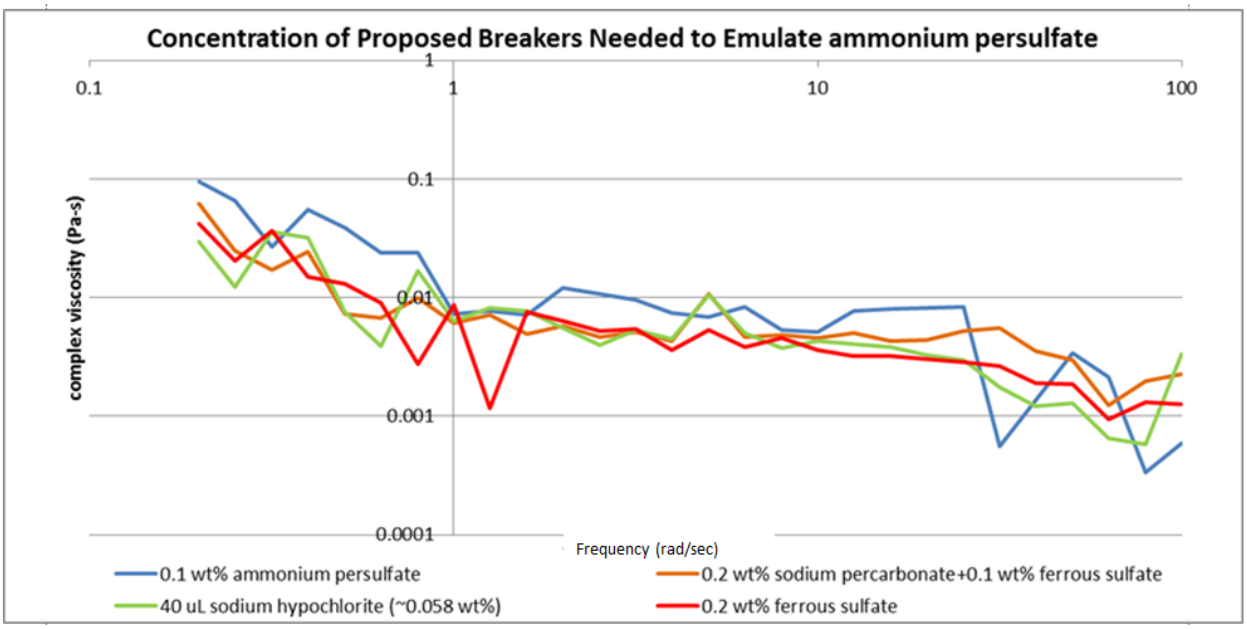

Figure 14: Frequency sweeps of each effective breaker at concentrations necessary to emulate ammonium persulfate acting on crosslinked guar at 50˚C.

This plot is important because it shows that these alternative breakers can provide the same degree of breaking as ammonium persulfate when used in higher concentrations. More concentrations were tested, with additional results is the appendix.

Filter-Degradation Study

Figure 15, below, shows the average percent permeate left on filter paper after filtration and drying described in the methods section. The total weight of guar and crosslinker in a 10 mL sample of crosslinked guar is 0.07 grams, 0.05 grams form guar and 0.02 grams from sodium tetraborate crosslinker. Percent permeate was calculated by subtracting the residual weight left on the filter from this maximum value to determine the mass that permeated the filter, then dividing by the maximum value and multiplying by 100 to get the percentage of the total that passed through the filter. Tests were conducted for each breaker found to be effective at decreasing fluid viscosity.

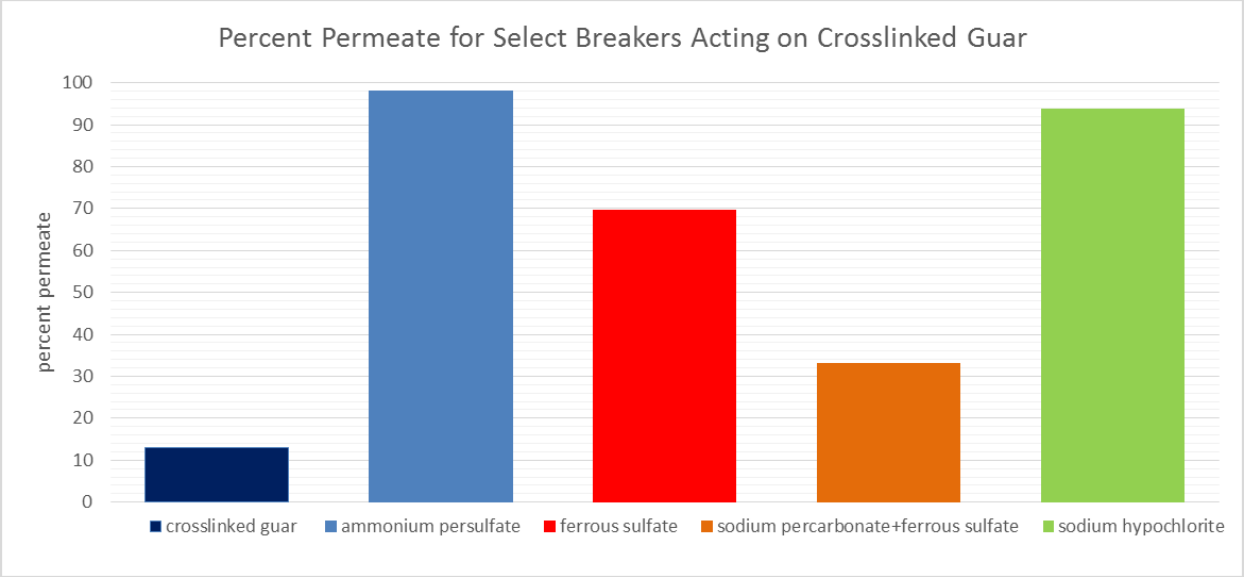

Figure 15: Percent permeates from filter-degradation studies

Ammonium persulfate most effectively breaks crosslinked guar into fragments small enough to pass through the filter, but is closely followed by sodium hypochlorite (still only 0.029 wt%). It's interesting to note that at 50˚C ferrous sulfate alone is more effective than when mixed with sodium percarbonate, a departure from the results of rheological studies at 50˚C. The mixture of sodium percarbonate with ferrous sulfate only breaks 33% of the polymer to a point that it can pass through the filter on average. Note that even with pure crosslinked guar 13% of the polymer still passes through. Individual trials used to generate these results can be viewed in the appendix.

Hazard Analysis

Each effective breaker (same as those analyzed in depth above) was analyzed in terms of relative toxicity with results displayed in Table 1.

Table 1: Negative health and environmental impacts of each viable breaker

Breaker	Effects
ammonium persulfate	acute toxin (oral LD_{50}: 700 mg/kg, dermal LD_{50}: 2000 mg/kg); eye, skin, and respiratory irritant; immunosuppressant; damage to gastrointestinal tract; acute and chronic aquatic toxin (LC_{50} for fish: 76 mg/L for 96 h)
sodium percarbonate	oral rat LD50: 4090 mg/kg; inhalation rat LC50: 2300 mg/m3/2H. Eye, skin, and respiratory irritant.
sodium hypochlorite	toxic to aquatic life. 96-hour LC50: fathead minnows: 0.090-5.9 mg/L, bluegill sunfish: 0.10-2.48 mg/L. Eye, skin, and respiratory irritant. Highly corrosive upon ingestion.
ferrous sulfate	eye, skin, and respiratory irritant.

Ammonium persulfate is the most dangerous of these chemicals upon human ingestion or dermal contact. Unfortunately, sodium hypochlorite is far more toxic in aquatic environments. Since a major concern related to fracking is the fear of fracking fluid negatively impacting aquatic ecosystems, sodium hypochlorite was not further considered in the following section, despite its impressive ability to break down guar and crosslinked guar polymers at lower concentrations than ammonium persulfate. Sodium percarbonate is only marginally less toxic than ammonium persulfate, whereas ferrous sulfate has no known major health or environmental impacts.

Cost Analysis

Each of the remaining effective breakers was compared on the basis of bulk cost (as of August 12, 2016), as displays in Table 2, below.

Table 2: The bulk cost of each effective breaker

Breaker	Cost (dollars/metric ton)
ammonium persulfate	500
sodium percarbonate	450
ferrous sulfate	70

Both sodium percarbonate and ferrous sulfate are less expensive than ammonium persulfate in bulk, but the figure above doesn't account for the fact that more of these chemicals is needed to achieve the same degree of breaking as ammonium persulfate. About double the concentration (by weight) is need for either ferrous sulfate or sodium percarbonate with ferrous sulfate to achieve the same degree of breaking as ammonium persulfate. For the mixture of sodium percarbonate with ferrous sulfate, this makes the estimated cost to fully replace ammonium persulfate about $970 per equivalence, compared to $500 associated with 1 metric ton of ammonium persulfate. Ferrous sulfate alone is a far better economic choice because even with double the amount, the proportional cost is only about $140 compared to the same $500 cost for one metric ton of ammonium persulfate.

Conclusions

Summary

Eight potential replacements to ammonium persulfate as breaker in crosslinked guar hydraulic fracturing systems were proposed. Ammonium persulfate is highly toxic to humans and aquatic ecosystems, so replacing it with a less harmful alternative would be an exciting development in a time where enhanced energy recovery is a necessity. Each breaker was first rigorously tested to determine if it could reduce fluid viscosity to the same degree as ammonium persulfate. Breakers that approached the breaker ability of the conventional breaker were further analyzed in filter-degradation tests, hazard analyses, and cost analyses.

Contribution and Suggestions

Most of these potential replacements have never been tested before. Testing breakers on the basic of their radical forming potential instead of only considering oxidizing ability is entirely novel, but unfruitful. Additionally, stronger oxidizers used in bleach and detergent, such as sodium percarbonate and sodium hypochlorite, have not been widely tested in fracking systems. The use of iron catalyst to enhance oxidation by catalyzing radical formation is a novel contribution, as well as the discovery of ferrous sulfate as an effective, low cost breaker in its own right.

Based on the results of this study, ferrous sulfate (0.2 wt%) and sodium hypochlorite (~0.0029 wt%), as well as the combination of sodium percarbonate (0.2 wt%) catalyzed by ferrous sulfate (0.1 wt%) can achieve the same magnitude of breaking as ammonium persulfate. In residue tests sodium hypochlorite is the most competitive breaker, allowing only 4% less polymer to filter than ammonium persulfate. Ferrous sulfate alone and with sodium percarbonate are less effective at breaking crosslinked guar down to filterable components.

Despite its impressive breaking ability, sodium hypochlorite was discarded as a potential replacement upon hazard analysis. It's simply too toxic within aquatic ecosystems to be seriously considered. Even trace amounts can kill off entire populations of fish and other aquatic organisms.

Ferrous sulfate and the combination of sodium percarbonate with ferrous sulfate were further analyzed against ammonium persulfate in terms of cost. Sodium percarbonate can be purchased in bulk at a similar price to ammonium persulfate, but near double the concentration is needed, making the bulk cost of breaking with this chemical in combination with ferrous sulfate nearly double that of

breaking with ammonium persulfate. Ferrous sulfate is considerably less expensive. It appears that ferrous sulfate could be an effective replacement for ammonium persulfate in terms of its similar breaker ability, lesser toxicity, and lesser cost.

This begs the question: Why not use ferrous sulfate as the breaker in fracking wells? It's less toxic and less expensive than the conventional breaker while achieving the same effect at 50˚C with only marginally increased concentration. The problem may be that ferrous sulfate is the only compound proposed that does not follow the trend of being more active at higher temperature. This could pose a serious problem, especially since many wells have down-well temperatures well above 50˚C and this increase in temperature is known to only increase the activity of ammonium persulfate [3]. Additionally, solutions broken with ferrous sulfate are qualitatively different from all other solutions tested. Solutions broken with ferrous sulfate appear to have an increased cohesion property. This anomaly was not analyzed by any quantitative means in this study, but could point to a different breaker mechanism.

Future Work

Future studies into the effects of higher temperatures on the most impactful of the suggested breakers would be useful. If the trend of decreased activity with higher temperature continues for ferrous sulfate, it would easily be discarded as an effective breaker. Furthermore, the effectiveness of ferrous sulfate as a catalyst at higher temperatures is yet to be studied with either sodium percarbonate or ammonium persulfate.

Further rheological studies, analyzing storage and loss modulus of solutions broken with ferrous sulfate compared to other breakers would be useful. Ferrous sulfate broken solutions are qualitatively different from all others and analysis of the quantitative differences underlying would be interesting.

Tests to determine the relative abundance of hydroxyl radical in aqueous systems would be useful as well. Perhaps a link can be drawn more clearly between the relative abundance of hydroxyl radical formed by a breaker in aqueous solution and the breaker's ability to break crosslinked guar. Methods of GC/MS and UV-vis spectroscopy have been implemented in previous studies to determine relative radical abundance [13] [14].

References

[1] Ground Water Protection Council and ALL Consulting, “Modern Shale Gas Development in the United States: A Primer, 2009”.

[2] Congressional Research Service, "Unconventional Gas Shales: Development, Technology, and Policy Issues," U.S. Government, Washington, 2009.

[3] M. Sarwar, K. E. Cawiezel and H. A. Nasr-El-Din, "Gel Degradation Studies of Oxidative and Enzymatic Breakers to Optimize Breaker Type and Concentration for Effective Break Profiles at Low and Medium Temperature Ranges," Society of Petroleum Engineers, 2011.

[4] A. Granberg, Artist, Fracking Diagram. [Art]

[5] Halliburton, “Fracturing Fluid Systems: Broad Variety of Systems Enable Customizing the Treatment Fluid to Reservoir Requirements”, 2013.

[6] Aqualon, “Guar and Guar Derivatives”, Hercules, Incorporated, 2007.

[7] R. Prud'homme, V. Constien and S. Knoll, “The Effects of Shear History on the Rheology of Hydroxypropyl Guar Gels, Polymers in Aqueous Media” (vol 223), 1989, pp. 89-112

[8] E. Wattenberg, J. Bielicki, A. Suchomel, J. Sweet, E. Void and G. Ramachandran, "Assessment of the Acute and Chronic Health Hazards of Hydraulic Fracturing Fluids", Journal of Occupational and Environmental Hygiene, vol. 12, no. 9, pp. 611-624, 2015.

[9] Halliburton, "Best Practices: Fracturing Fluid Breakers," 2005.

[10] H.D. Brannon and R.M. Tjon-Joe-Pin, “Biotechnological Breakthrough Improves Performance of Moderate to High-Temperature Fracturing Applications”. Paper presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, 25-28 September, 1994. Society of Petroleum Engineers 28513-MS.

[11] N. Milne, “Oxygen bleaching systems in domestic laundry”, Journal of Surfactants and Detergents, vol 1, issue 2, pp 253-261, 1998.

[12] K. Barbusinski, “Fenton Reaction- Controversy Concerning the Chemistry”. Ecological Chemistry and Engineering, Vol 16, No. 3, 2009.

[13] N. Nilvebrant, M. B. Jansson, “Hydroxyl radical formation during hydrogen peroxide bleaching”. STFI-Packforsk, Report No. 197, 2005.

[14] M. Sahni, B. R. Locke, “Quantification of Hydroxyl Radicals Produced in Aqueous Phase Pulsed Electrical Discharge Reactors”. Industrial and Engineering Chemistry Research, 45 (17), pp 5819-5825, 2006.

[15] Rutgers GenChem, “Putty and Slime: Molecular Structure and Properties”. http://genchem.rutgers.edu/putty.html, 2008.

[16] MiniScience.com, “Make Guar Gum Slime (Polymers)”. http://www.miniscience.com/projects/slime/GuarGumSlime.html.

[17] Ferraris, Chiara F., RILEM International Symposium on "The Role of Admixtures in High Performance Concrete", Monterrey, Mexico, March 21-26, 199

Appendix

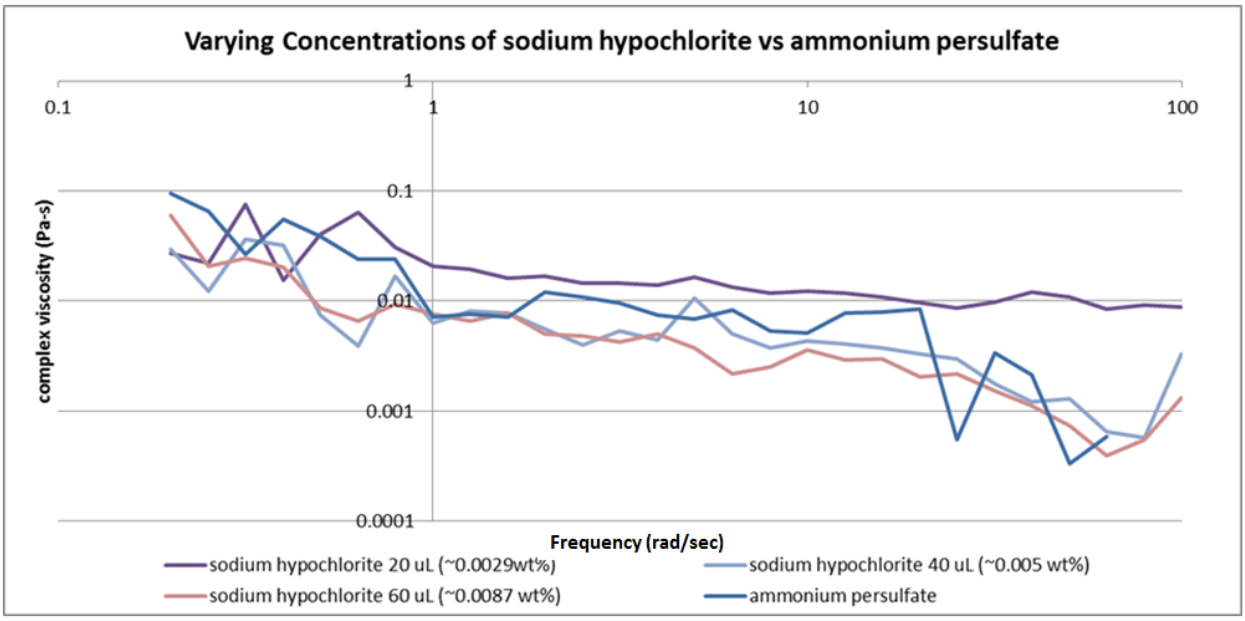

Figure A1: Frequency sweep of crosslinked guar broken with various concentrations of sodium hypochlorite at 50˚C

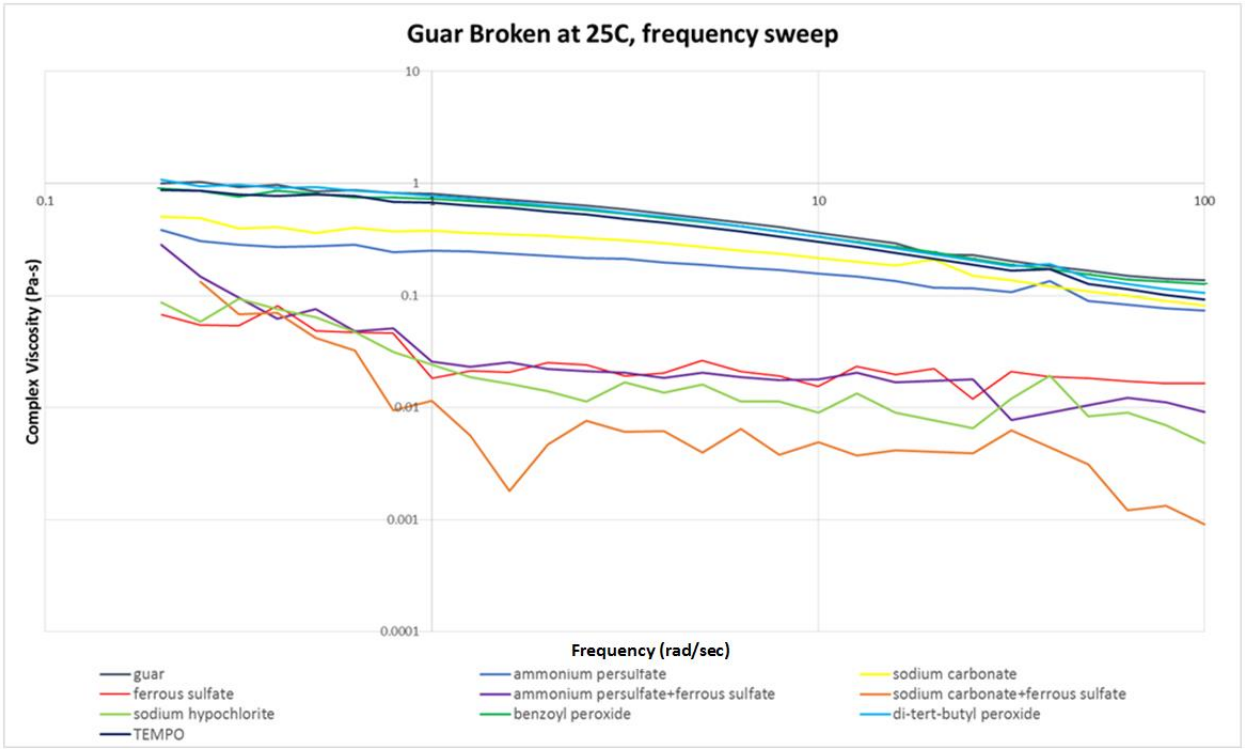

Figure A2: Frequency sweep of guar broken with various breakers at 25˚C

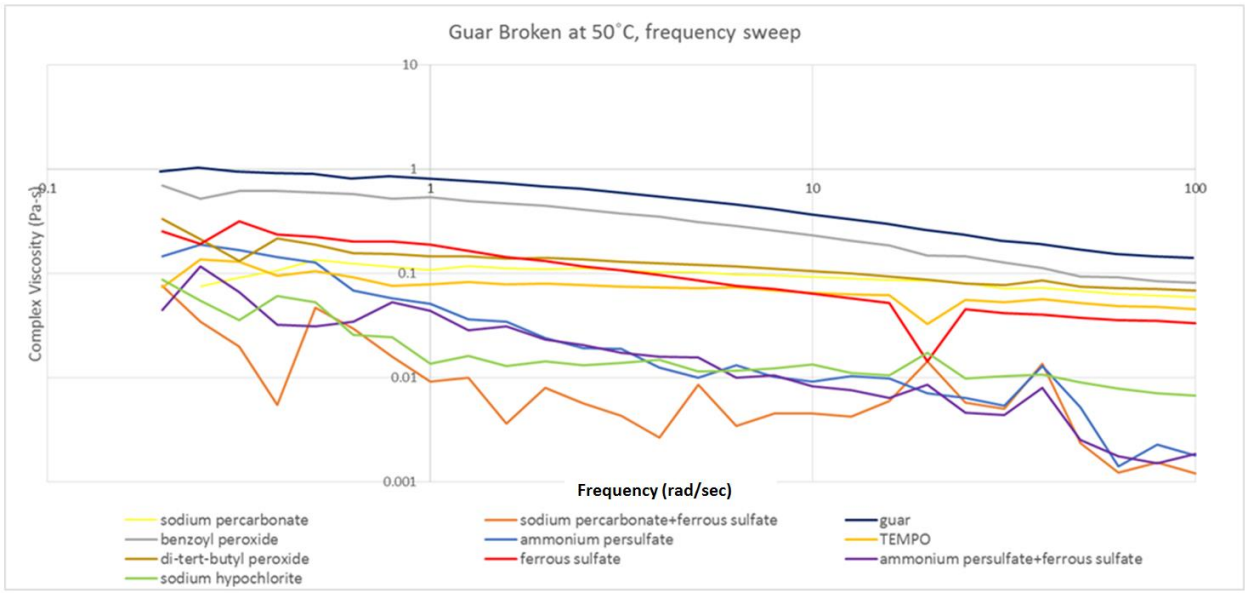

Figure A3: Frequency sweep of guar broken with various breakers at 50˚C

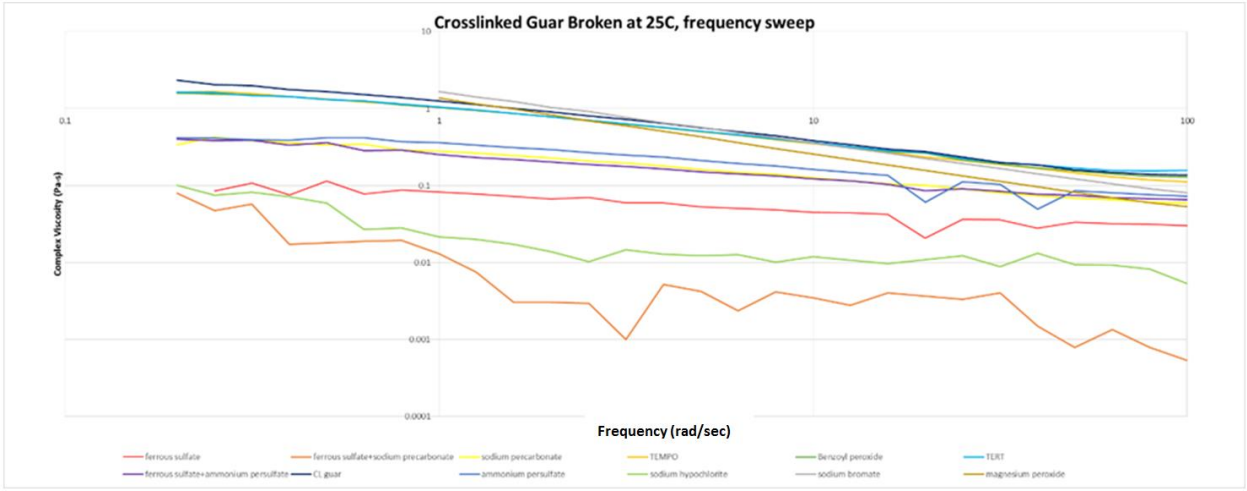

Figure A4: Frequency sweep of crosslinked guar broken with various breakers at 25˚C

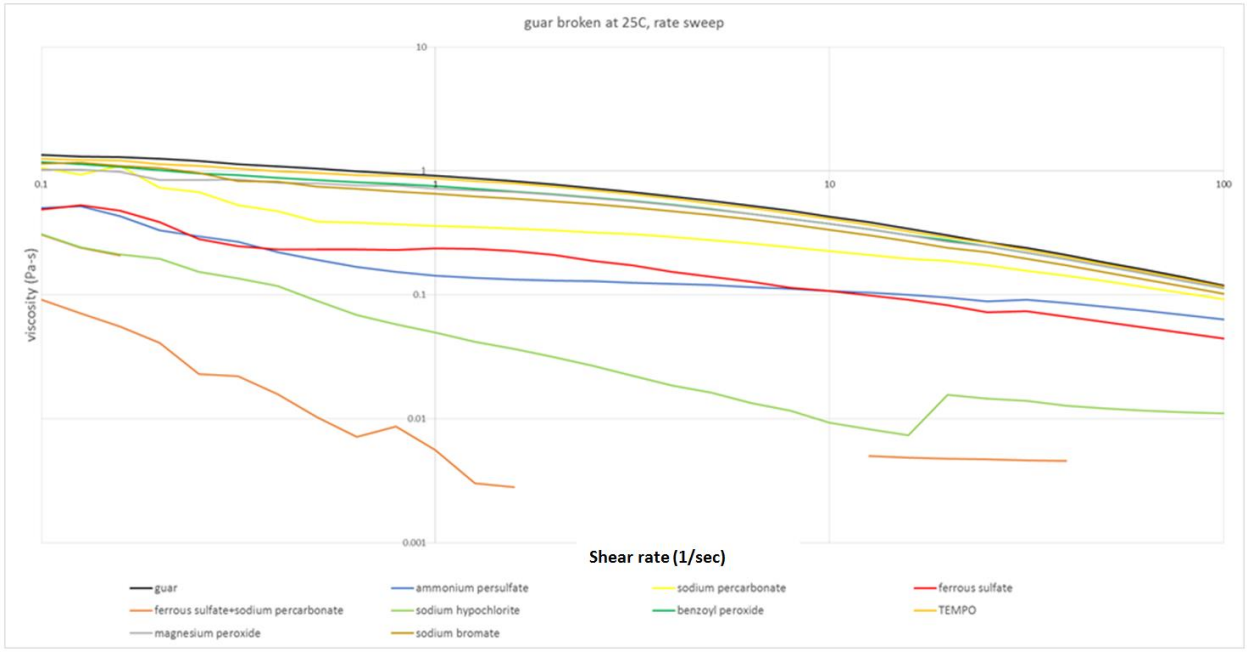

Figure A5: Rate sweep of guar broken with various breakers at 25˚C

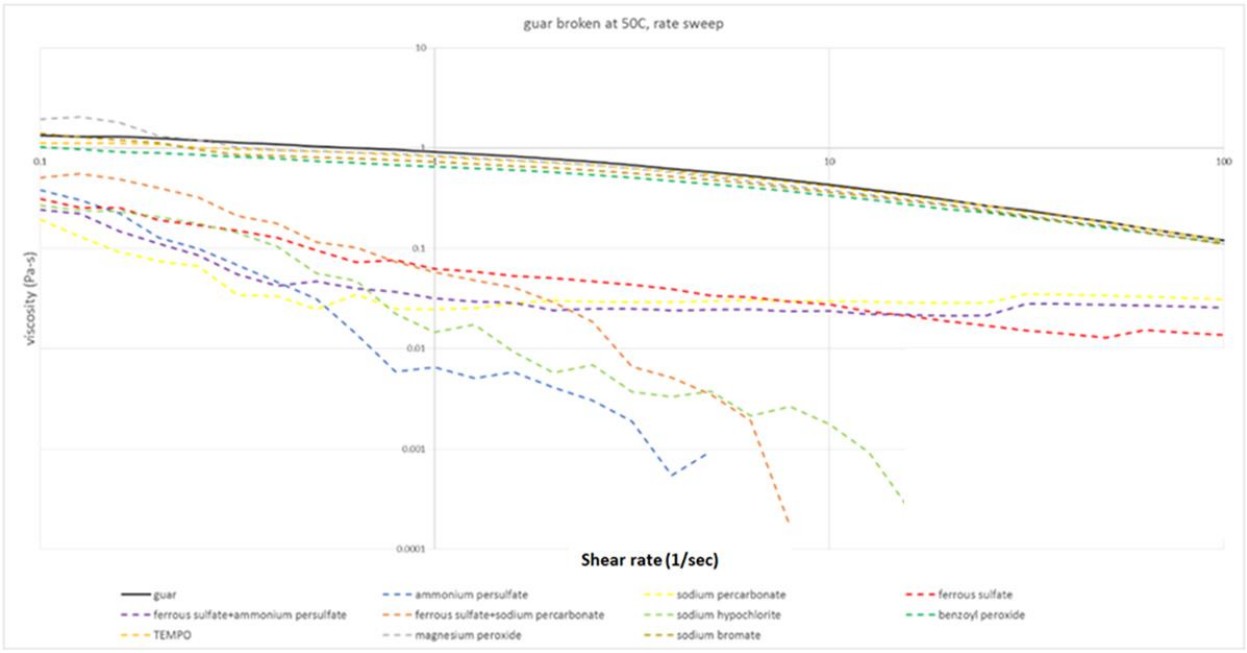

Figure A6: Rate sweep of guar broken with various breakers at 50˚C

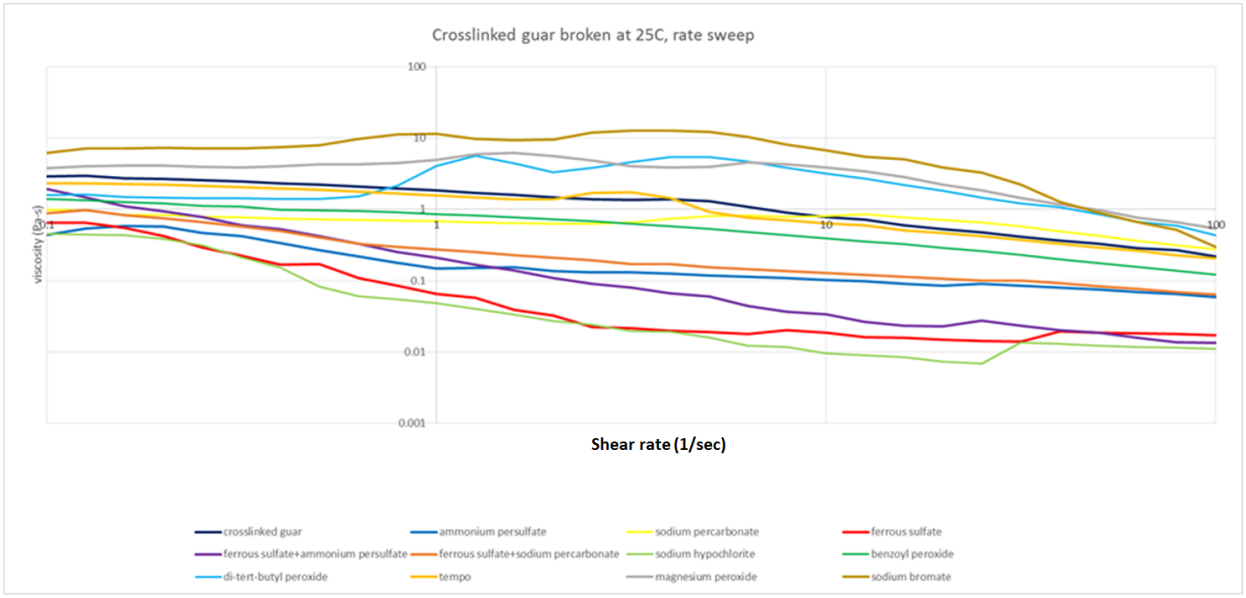

Figure A7: Rate sweep of crosslinked guar broken with various breakers at 25˚C

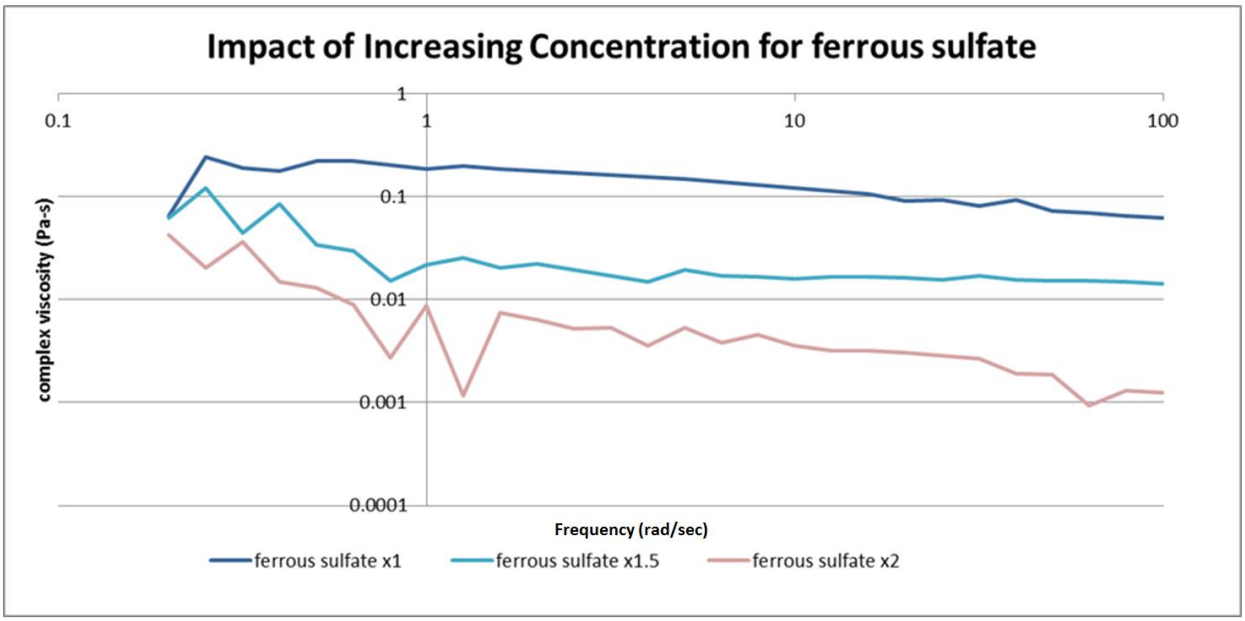

Figure A8: Frequency sweep of crosslinked guar broken with various concentrations of ferrous sulfate at 50˚C

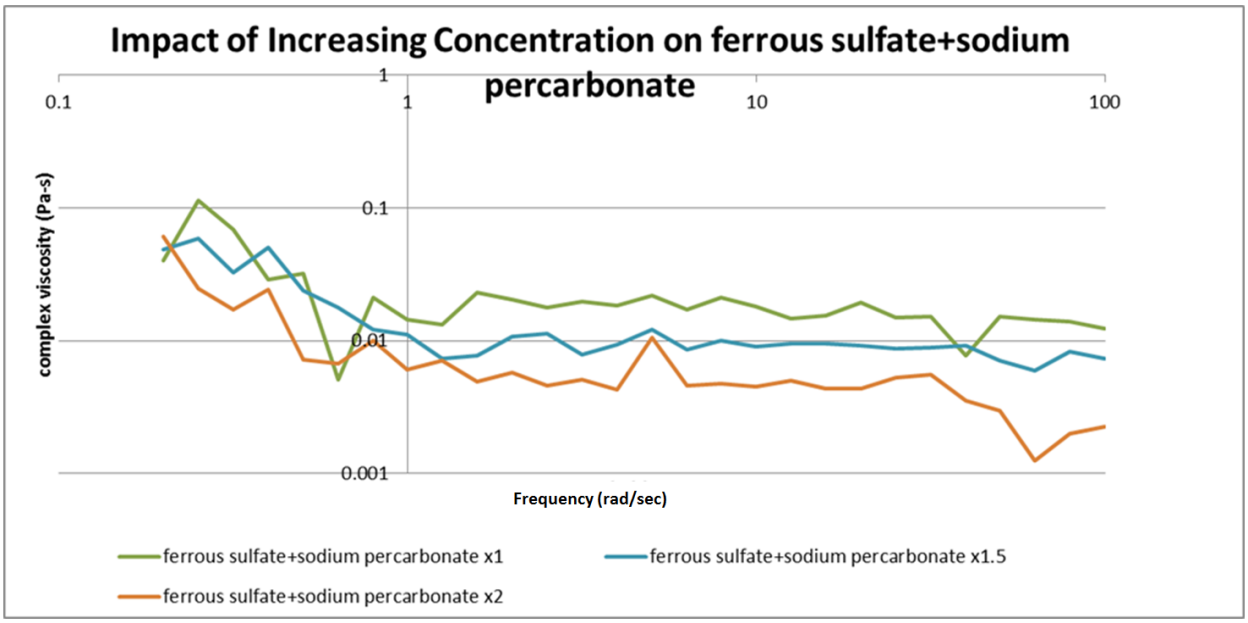

Figure A9: Frequency sweep of crosslinked guar broken with various concentrations of ferrous sulfate+sodium percarbonate at 50˚C

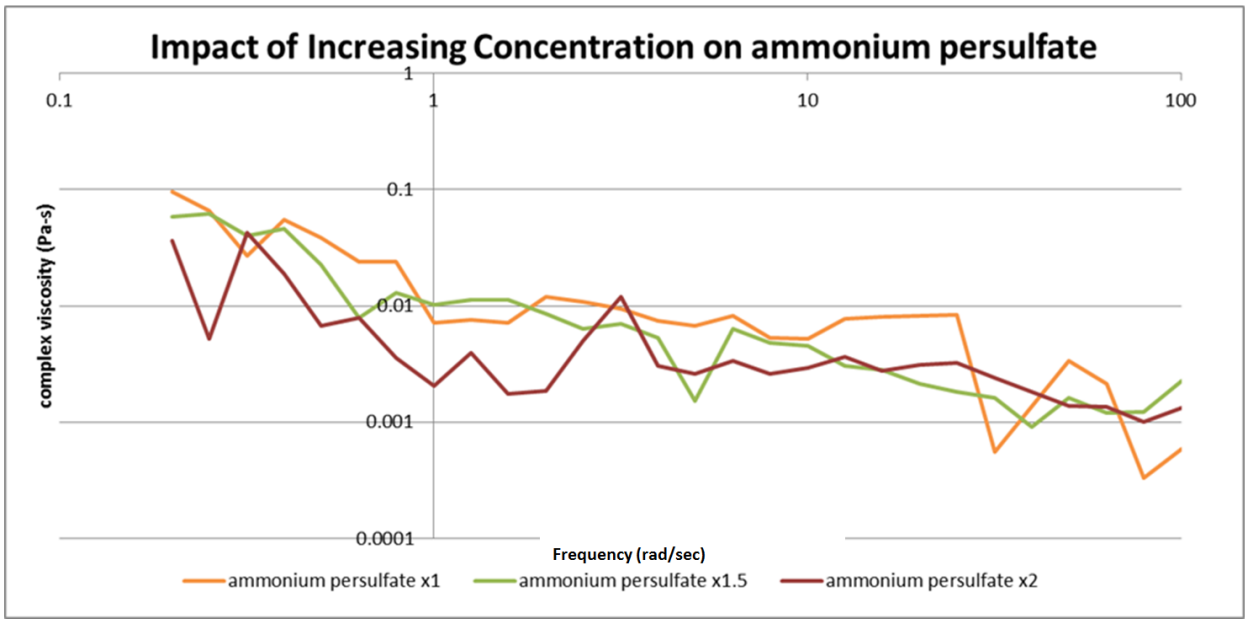

Figure A10: Frequency sweep of crosslinked guar broken with various concentrations of ammonium persulfate at 50˚C

Table A1: Data table for filter-degradation study displaying individual trials.

Trial #	crosslinked guar	ammonium persulfate	ferrous sulfate	sodium percarbonate +ferrous sulfate	sodium hypochlorite
1	0.098g	0.008g	0.0177g	0.0489g	-0.0016g
2	0.0367g	-0.002g	0.0176g	0.0477g	0.016g
3	0.0481g	-0.0021g	0.0284g	0.0439g	-0.0016g
average	0.0609g	0.0013g	0.0212g	0.0468g	0.00427g
Percent permeate	13%	98.1%	69.7%	33.1%	93.9%